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Heterocyclic Systems in Dye Chemistry

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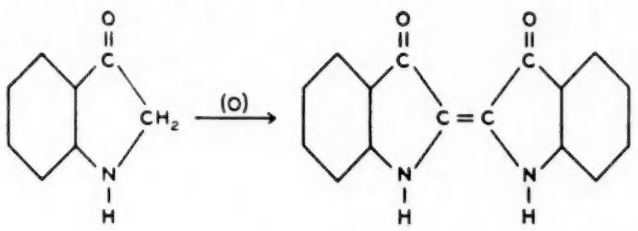
It is generally recognized that compounds of the azo type constitute by far the largest single class of dyestuffs, and the majority of them are derived from the relatively simple aromatic amines and phenols containing homocyclic systems.

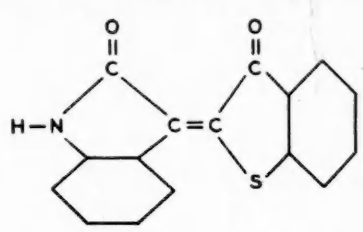
During recent years, a great deal of attention has been directed to other classes of dyestuffs, chiefly those derived from heterocyclic systems containing nitrogen, oxygen, or sulfur. In this article some of the more common classes of these dyes are grouped and discussed according to the nature of the heterocyclic system involved.

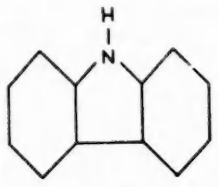
Simple indole derivatives, such as indole itself, indoxyl, isatin, etc., are practically colorless; however, when oxidized, they double up to yield intensely colored indigos—exceedingly good vat dyes. The following is an example:



By introducing various substituents as halogen, alkoxy, and alkyl groups into the indoxyl nucleus, a wide variety of dyes is obtained.

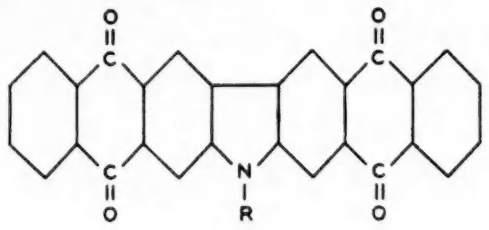
The thioindigos, in which sulfur replaces the NH groups of indigo, furnish dyes of an even greater range of color. It is only necessary to give a single illustration to show the numerous possibilities which arise when unlike components are employed in generating the dyes. For example, a vivid scarlet dye having great affinity for wool is obtained by condensing one molecule of isatin with one of 3-hydroxythionaphthene (right):





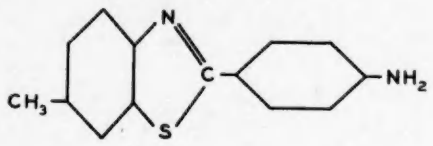
The carbazole ring system (left), which might be called a benzoindole is the parent substance of some of the fastest blue vat dyes which in many cases have replaced the indigos. These dyes are prepared by condensing a substituted carbazole with nitrosophenol in sulfuric acid and submitting the product to a sulfur melt.

A class of yellow dyes having the following structure,

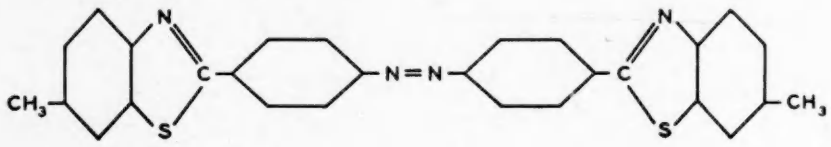


is obtained by the condensation of a nitrogen alkyl substituted carbazole with phthalic anhydride.

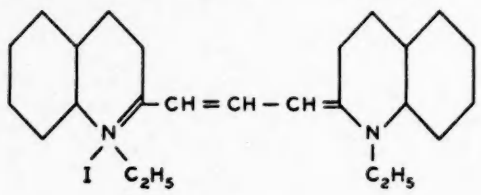
A very large group of azo dyes is derived from intermediates containing the benzothiazole ring system, of which 2-(p-aminophenyl)-6-methyl benzothiazole, having the formula—



is among the most important. One of the fastest yellow dyes known is prepared by oxidizing this compound with hypochlorite to the azo dye:

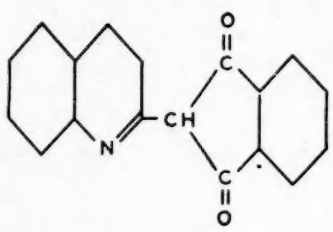


An important class of heterocyclic systems containing six members in the ring includes the quinoline derivatives. Many valuable photographic sensitizing dyes, such as pinacyanole,



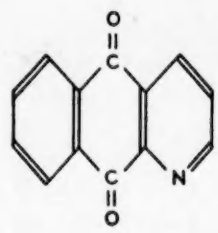
are representative of this group.

Adding or altering various substituents, increasing the length of the conjugated chain, and, especially, introducing two unlike heterocyclic systems into the molecule, afford a wide range of dyes.



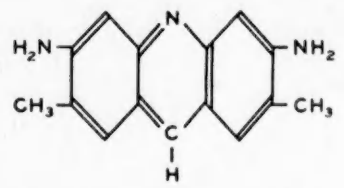
From quinophthalone (Quinoline Yellow) (left) is obtained, after sulfonation, the sodium salt of its disulfonic acid. This latter, unlike the photosensitizing dyes, is very resistant to light and is used extensively for dyeing wool and silk brilliant greenish-yellow shades.

The azanthraquinones (left, top next column) which contain the pyridine ring

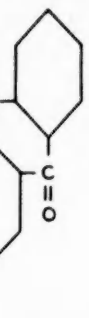


system serve as intermediates for dyes analogous to those of the well known and widely used anthraquinone series.

The acridines are of considerable importance and might well be classified as benzoquinoline derivatives. Acridine yellow (below), which is typical of this group, is prepared simply by the action of formaldehyde on 2,4-diaminotoluene, followed by mild oxidation of the diaminodimethyl hydroacridine thus formed. By alkylating the amine groups, much deeper shades are obtained.

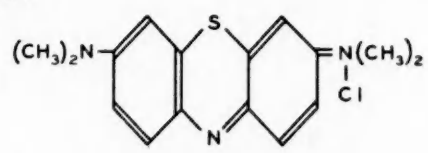


More complex dyes of the acridone series, with the anthraquinone ring and the structure below,

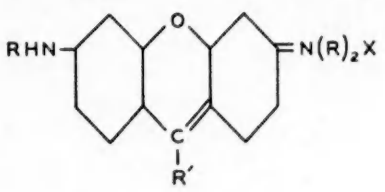


have proved to be fast blue vat dyes.

The thiazines form a class of dyes of which methylene blue is one of the most common:



The oxazines have the same structure as the thiazines, with one exception: namely, they have oxygen instead of sulfur in the ring. The well known Meldola's Blue and the large class of gallocyanines fall into this group.



(X is negative radical)
(R is alkyl group)
(R′ is aryl group)

Pyronines,

which do not contain any ring nitrogen, can be considered as derivatives of the anhydride of 2,2′-dihydroxy diphenylmethane. They furnish the valuable Rhodamines having the constitution indicated in the example at bottom of second column, page 2.

This brief survey is by nc means complete but merely calls attention to some of the more simple dyes which are commonly used. A comprehensive study of the subject would include the quinoxalines, pyrazolones, benzimidazoles, benzoxazoles, isoxazolones, and other more complex heterocyclic ring systems which are employed extensively in the preparation of dyes. It would also include the numerous valuable vat dyes of unknown structure obtained by the sulfur melt of intermediates.

With the rapid expansion of the organic chemical industry and with the new heterocyclic intermediates which are now cheap and abundant, many interesting and important developments in dye chemistry can be expected.

Eastman Organic Chemicals as Analytical Reagents

XLVI REAGENTS FOR GOLD

Dimethylglyoxime

Thompson, Beamish, and Scott. *Ind. Eng. Chem., Anal. Ed.* 9,420 (1937)

Gold may be determined quantitatively by means of dimethylglyoxime. The solution containing gold is made to 50 cc. and acidified with about 0.5 cc. of concentrated hydrochloric acid. To this are added 100 mg. of dimethylglyoxime as a 1% solution in alcohol, and the yellow precipitate allowed to form. The mixture is then boiled for 30 minutes, and the gold precipitate filtered through a filtering crucible and washed with water. The residue is finally burned and weighed as gold.

Hydroquinone

Beamish, Russell, and Seath. *Ind. Eng. Chem., Anal. Ed.* 9,174 (1937)

A 1% aqueous solution of hydroquinone precipitates gold rapidly and completely. The gold is dissolved in aqua regia, evaporated to dryness, and finally taken up in hydrochloric acid. The filtered solution is made to 50 cc., brought to a boil, and the gold precipitated by the addition of 1% aqueous hydroquinone; an excess of the reagent is then added. After boiling for 20 minutes, the mixture is filtered through a porous-bottomed filtering crucible. The precipitate is washed with hot water, burned, and weighed.

By this method gold can be separated from platinum and palladium, since occlusion is negligible. Copper, nickel, and zinc do not interfere. The filtrate obtained from the gold precipitation may be used for the determination of platinum and palladium.

4,4′-Tetramethyldiaminotriphenylmethane

Kul'berg. *Zavodskaya Lab.* 5,170 (1936); *Chem. Abst.* 30,4782 (1936)

As little as .003 mg. of gold may be determined colorimetrically in the presence of copper, by means of 4.4′-tetramethyldiaminotriphenylmethane (leuco malachite green). The unknown solution is buffered with sodium acetate and acetic acid to pH 3.6. The reagent is prepared by adding 0.5 cc. of 80% acetic acid to 0.5 gms. of the leuco dye in 5 cc. of alcohol, boiling for from 3 to 5 minutes, and diluting with 10 cc. of alcohol and 35 cc. of the buffer solution. To the unknown and to standard solutions, which are run concurrently, are added 1 cc. portions of the reagent, and the colors compared.

Sixty-six New Eastman Organic Chemicals

4638	β-Alanine
4621	ε-Amino-n-caproic Acid
4474	Ammonium Rhodanilate
4610	n-Amyl Succinate
4640	Ascorbic Acid
T 1602	Benzyl Disulfide (Techn.)
4636	5-Bromo-2-aminotoluene
4615	p-Bromo-iso-butylbenzene
4620	p-Bromo-iso-propylbenzene
4631	p-Bromo-n-propylbenzene
P 4583	p-tert.-Butylcatechol (Pract.)
P 4606	iso-Butyl Crotonate (Pract.)
T 4622	sec.-Butyl Glycolate (Techn.)
T 3483	n-Butyl Sebacate (Techn.)
4609	n-Butyl Succinate
4644	Cellulose Acetate (acetone-soluble) (Low Viscosity, High Acetyl)
4650	Cellulose Acetate (acetone-soluble) (Low-Medium Viscosity, High Acetyl)
4655	Cellulose Acetate (acetone-soluble) (High-Medium Viscosity, Low Acetyl)
4660	Cellulose Acetate (acetone-soluble) (High Viscosity, Low Acetyl)
4623	Cellulose Acetate Butyrate (16% Butyryl)
4642	Cellulose Acetate Hydrogen Phthalate
4632	Cellulose Acetate Propionate (16% Propionyl)
4531	Cellulose Acetate Stearate
4303	Citraconic Anhydride
T 4613	Diaminostilbenedisulfonic Acid (Techn.)
T 4436	Diamylnaphthalene (Techn.)
4616	Dibenzylacetic Acid
4344	2,5-Dibromotoluene
P 1440	p,p′-Dichlorobenzophenone (Pract.)
T 4581	2,5-Dichlorophenylhydrazine-4-sulfonic Acid (Techn.)
P 4641	Dicyclohexyl (Pract.)
P 4627	Dicyclohexylamine (Pract.)
T 4580	Diethylene Dilaurate (Techn.)
T 4573	Diethylenetriamine (Techn.)
T 4625	4,4′-Dihydroxybenzophenone (Techn.)
P 4299	2,5-Dihydroxydiphenyl (Pract.)
T 4624	3,4-Dihydroxydiphenyl (Techn.)
P 98	Dimethylglyoxime (Pract.)
4645	s-Dimethyl-p-phenylenediamine Dioxalate
4020	Esculin
4634	p-Ethoxybenzoic Acid
P 2201	Ethyl Glycolate (Pract.)
P 2851	Ethyl Orthoacetate (Pract.)
P 2858	Ethyl Orthopropionate (Pract.)
T 4571	Fenchone (Techn.)
735	Fluorescein Sodium Salt
P 1518	Guanidine Nitrate (Pract.)
P 902-X	Hydrazine Hydrate (85% in water) (Pract.)
P 985	p-Hydroxybenzaldehyde (Pract.)
T 873	Lauryl Alcohol (Techn.)
P 3573	Methyl Acrylate (Pract.) (Stabilized with Hydroquinone)
2760	2-Methylbenzimidazole
4575	5-Methylbenzimidazole
4533	α-Methyl-α-phenylhydrazine Sulfate
4215	α-Naphthaleneacetic Acid
2694	α-Naphthoflavone
4554	3-Nitro-2-aminotoluene
2408	p-Nitrobenzaldehyde
4550	4-Nitro-2-chlorophenol
4617	Phenylethylacetic Acid
P 4374	iso-Propyl Glycolate (Pract.)
4618	dl-Serine
P 4380	1-p-Sulfophenyl-3-methyl-5-pyrazolone (Pract.)
T 4598	1, 2, 3, 4-Tetrachlorobenzene (Techn.)
4619	dl-Threonine
T 4572	Triethylenetetramine (Techn.)